<Division of Multidisciplinary Chemistry>Molecular Aggregation Analysis

Division of Multidisciplinary Chemistry
– Molecular Aggregation Analysis –

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Scope of Research

We design and synthesize unique electronic materials with sophisticated device applications in mind. These materials have novel solid-state aggregation structures or well-defined interface orientation that promote efficient electrical current flow or enhance device lifetime. Electronic devices based on these new materials are then evaluated using advanced measurement techniques, and the results are used to inform the next direction of the materials chemistry. We call this synergistic approach for achieving our research goals "Needs Inspired Fundamental Science".

KEYWORDS
Molecular Design and Synthesis
Functional Materials
Perovskite Solar Cells
Molecular Aggregation
Semiconductors

Selected Publications

Ozaki, M.; Shimazaki, A.; Jung, M.; Nakaike, Y.; Maruyama, N.; Yakumaru, S.; Rafieh, A. I.; Sasamori, T.; Tokitoh, N.; Ekanayake, P.; Murata, Y.; Murdey, R.; Wakamiya, A., A Purified, Solvent-Intercalated Precursor Complex for Wide Process Window Fabrication of Efficient Perovskite Solar Cells and Modules, *Angew. Chem. Int. Ed.*, **58,** 9389-9393 (2019).

Ozaki, M.; Ishikura, Y.; Truong, M. A.; Liu, J.; Okada, I.; Tanabe, T.; Sekimoto, S.; Ohtsuki, T.; Murata, Y.; Murdey, R.; Wakamiya, A., Iodine-rich Mixed Composition Perovskites Optimised for Tin(IV) Oxide Transport Layers: the Influence of Halide Ion Ratio, Annealing Time, and Ambient Air Aging on Solar Cell Performance, *J. Mater. Chem. A*, **7,** 16947-16953 (2019).

Nakamura, T.; Shioya, N.; Shimoaka, T.; Nishikubo, R.; Hasegawa, T.; Saeki, A.; Murata, Y.; Murdey, R.; Wakamiya, A., Molecular Orientation Change in Naphthalene Diimide Thin Films Induced by Removal of Thermally Cleavable Substituents, *Chem. Mater.*, **31,** 1729-1737 (2019).

Truong, M. A.; Lee, J.; Nakamura, T.; Seo, J.-Y.; Jung, M.; Ozaki, M.; Shimazaki, A.; Shioya, N.; Hasegawa, T.; Murata, Y.; Zakeeruddin, S. M.; Gratzel, M.; Murdey, R.; Wakamiya, A., Influence of Alkoxy Chain Length on the Properties of Two-Dimensionally Expanded Azulene Core-Based Hole-Transporting Materials for Efficient Perovskite Solar Cells, *Chem. Eur. J.*, **25,** 6741-6752 (2019).

Ozaki, M.; Nakaike, Y.; Shimazaki, A.; Jung, M.; Maruyama, N.; Yakumaru, S.; Rafieh, A. I.; Ekanayake, P.; Saito, T.; Shimakawa, Y.; Sasamori, T.; Murata, Y.; Murdey, R.; Wakamiya, A., How to Make Dense and Flat Perovskite Layers for >20% Efficient Solar Cells: Oriented, Crystalline Perovskite Intermediates and their Thermal Conversion, *Bull. Chem. Soc. Jpn.*, **92,** 1972-1979 (2019).

Influence of Alkoxy Chain Length on the Properties of Two Dimensionally Expanded Azulene-Core-Based Hole-Transporting Materials for Efficient Perovskite Solar Cells

A series of two-dimensionally expanded azulenecore-based π systems have been synthesized with different alkyl chain lengths in the alkoxy moieties connected to the partially oxygen-bridged triarylamine skeletons. The thermal, photophysical, and electronic properties of each compound were evaluated to determine the influence of the alkyl chain length on their effectiveness as hole-transporting materials (HTMs) in perovskite solar cells (PSCs). All the synthesized molecules showed promising material properties, including high solubility, the formation of flat and amorphous films, and optimal alignment of energy levels with perovskites. In particular, the derivatives with methyl and *n*-butyl in the side chains retained amorphous stability up to 233 and 159 °C, respectively. Such short alkoxy chains also resulted in improved electrical device properties. The PSC device fabricated with the HTM with *n*-butyl side chains showed the best performance with a power conversion efficiency of 18.9%, which compares favorably with that of spiroOMeTAD-based PSCs (spiro-OMeTAD = 2,2',7,7'-tetrakis[N,Nbis(p-methoxyphenyl)amino]-9,9'-spirobifluorene).

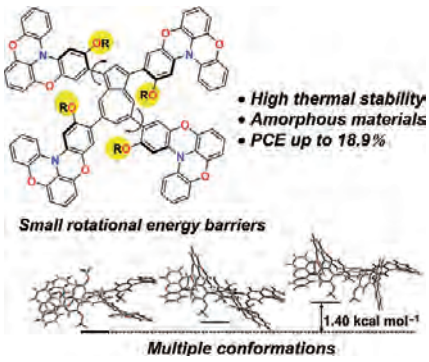

Figure 1. Molecular structures of the azulene-core-based two-dimensionally expanded π-system derivatives.

A Purified, Solvent-Intercalated Precursor Complex for Wide-Process Window Fabrication of Efficient Perovskite Solar Cells and Modules

A high-purity methylammonium lead iodide complex with intercalated dimethylformamide (DMF) molecules, $CH_3NH_3PbI_3 \cdot DMF$, is introduced as an effective precursor material for fabricating high-quality solution-processed perovskite layers. Spin-coated films of the solvent-intercalated complex dissolved in pure dimethyl sulfoxide (DMSO) yielded thick, dense perovskite layers after thermal annealing. The low volatility of the pure DMSO solvent extended the allowable time for low-speed spin programs and considerably relaxed the precision needed for the antisolvent addition step. An optimized, reliable fabrication method was devised to take advantage of this extended process window and resulted in highly consistent performance of perovskite solar cell devices, with up to 19.8% power-conversion efficiency (PCE). The optimized method was also used to fabricate a 22.0 cm^2, eight cell module with 14.2% PCE (active area) and 8.64 V output (1.08 V/cell).

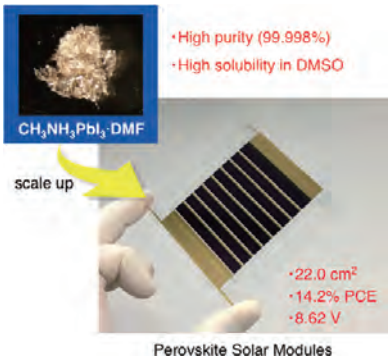

Figure 2. Photograph of $CH_3NH_3PbI_3 \cdot DMF$ complex and the perovskite solar modules.

Iodine-rich Mixed Composition Perovskites Optimized for Tin(iv) Oxide Transport Layers: the Influence of Halide Ion Ratio, Annealing Time, and Ambient Air Aging on Solar Cell Performance

Iodine-rich mixed composition metal–halide perovskites were developed to improve the performance of perovskite solar cell devices incorporating tin(IV) oxide substrates for electron transport layers by optimizing the I/Br halide ion ratio. Device performance was further enhanced by exposing to ambient atmosphere over several days, which correlated with a shift of the energy levels in the perovskite and significant suppression of charge carrier recombination. A high power conversion efficiency of 20.6% was obtained for the aged device.

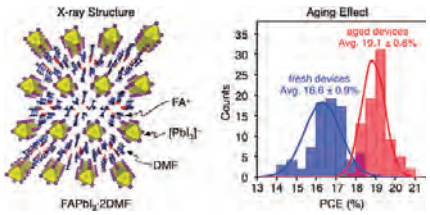

Figure 3. X-ray crystal structure of $FAPbI_3 \cdot DMF$ complex and the performance of perovskite solar cells.